

PATENT SPECIFICATION

(11) 1 505 402

1 505 402

- (21) Application No. 11001/75 (22) Filed 17 March 1975
 (23) Complete Specification filed 15 March 1976
 (44) Complete Specification published 30 March 1978
 (51) INT CL² C08F 2/22
 (52) Index at acceptance C3P 642 KT
 (72) Inventor DONALD ALFRED BENNETT



(54) PREPARATION OF GRAFT COPOLYMERS

(71) We, I.S.R. HOLDING, S.A.R.L., a Luxembourg Company, of 43, Rue Goethe, Luxembourg, Grand Duchy of Luxembourg, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the preparation of graft copolymers. In U.K. Patent Specification No. 1,373,089 there is described a continuous process for the preparation of graft copolymers, such as ABS, by grafting a vinyl or vinylidene aromatic monomer and an unsaturated nitrile monomer onto a latex of a rubber polymer selected from polybutadiene and butadiene-styrene copolymer.

In the process of U.K. Patent Specification No. 1,373,089 the mixture of latex and the monomers to be grafted is continuously supplied to a first stage, preferably after an imbibition period. The graft polymerisation is initiated in said first stage and polymerisation is continued at a fast conversion rate not exceeding 5% per minute to convert up to 65% of monomers to polymer. The reaction mixture is continuously removed from said first stage and supplied to at least a second stage and the graft polymerisation continued further to a conversion of at least 80% by weight of monomers to polymer. The temperature in each stage is 50° to 100°C and the temperature of imbibition (where imbibition is used) is 20° to 90°C. Each stage is preferably carried out in a stirred reactor.

In one aspect, the present invention is concerned with a modification of the process described in U.K. Patent Specification No. 1,373,089 in which a natural rubber latex replaces all or some of the polybutadiene or butadiene-styrene polymer latex. Broadly the present invention relates to the continuous preparation of graft polymers in two or more stages using one or more of a variety of monomers and employing natural rubber latex as the backbone polymer latex.

According to the present invention a continuous process for grafting natural rubber latex comprises (1) supplying the latex, one or more vinyl or vinylidene monomers to be grafted and polymerisation initiator to a first agitated reactor; (2) carrying out a proportion of the graft reaction in the first reactor; (3) continuously removing reaction mixture from the first reactor to a second agitated reactor; (4) continuing the graft reaction in the second reactor to a conversion of at least 85% by weight of the monomers to polymer and (5) removing the grafted latex from the second reactor, the conversion in the first reactor not exceeding 75%.

The natural rubber latex may be employed alone or with up to e.g. 50%, of another compatible latex, e.g. SBR latex or polybutadiene latex. Attention must be paid to the reaction conditions employed. The temperature of each reactor is from 40° to 100°C. However, it is preferred that the temperature of each reactor is within the range of 50° to 65°C. Above such temperatures (e.g., 85°C) care must be taken that coagulum does not form in unacceptable amounts. In some cases the temperature of each stage may be lower than 50°C. Generally below 35°C the grafting reaction proceeds at an unacceptably low rate. 40°C is therefore the lowest practicable temperature. Preferably the temperature of the second reactor is higher than that of the first. It is also preferred that initiator systems which are at least partly oil soluble are used in order to keep coagulum formation to as low a level as possible. A hydroperoxide-amine reaction initiator system is one preferred system. An example of such a system is t-butyl hydroperoxide (oil soluble) in combinations with tetraethylene pentamine (water soluble). Benzoyl peroxide is also a suitable initiator but is less preferred. As a further precaution against formation of coagulum it is desirable to add a small quantity of emulsifier in order

to increase the stability of the rubber latex. In U.K. Patent Specification No. 1,373,089 it is suggested that up to about 4 parts by weight (dry) per hundred parts of monomer plus latex of one or more anionic emulsifiers is used. A general example of a suitable anionic emulsifier is an alkali metal salt (usually a potassium or sodium salt) of a long chain carboxylic acid having e.g., 12 to 20 or more carbon atoms. In the present invention alkyl sulphates and alkyl or alkylaryl sulphonates may be used if desired. Preferably a secondary emulsifier, such as an alkali metal salt of naphthalene sulphonic acid derivatives, is included. Where a secondary emulsifier is used the weight ratio of secondary emulsifier to the main emulsifier may be quite high, e.g., 5:1 to 1:5. A secondary emulsifier is one which is a poor soap and poor at forming micelles but is however a good stabilizer for the micelles once formed. Such emulsifiers fall into a well defined category and in this respect reference may be made to Encyclopedia of Polymer Science & Technology Vo. 5 page 823 John Wiley & Sons 1966. Examples of preferred emulsifiers are potassium oleate, potassium rosinat, a mixture thereof and a mixture of potassium oleate and potassium linoleate with small amounts of other salts and similar salts as, for example, are described and claimed in U.K. Patent Specification No. 1,380,713. Where a fatty acid salt is employed as emulsifier, the use of a secondary emulsifier is particularly desirable. In the present invention the amount of emulsifier(s) used is up to 4 parts by weight (dry) per hundred parts of monomer plus latex, but the preferred amount may be lower, e.g. 0.5 to 2.0 parts. In some cases no addition of emulsifier is required.

Attention must also be paid to the pH of the reaction. The pH of reaction should be maintained in the alkaline range since otherwise complete coagulation of the latex would occur, but higher pHs, e.g., in the range 10 to 13, are preferred. The rubber to monomer ratio is determined to some extent by the final product which is desired. For a rubbery product the rubber to monomer weight ratio is at least 1:1, e.g., 1.5:1. For a thermoplastic product ratios of e.g., 1:5 may be used.

Examples of vinyl aromatic or vinylidene aromatic monomers which may be grafted on to the base latex comprising a natural rubber latex are styrene, alpha methyl styrene and ar-methyl styrenes such as vinyl toluene. Styrene, alpha methyl styrene and mixtures thereof are preferred. Examples of unsaturated nitrile monomers which may be used are short chain aliphatic nitriles such as acrylonitrile and methacrylonitrile. In one preferred embodiment of our invention styrene and acrylonitrile are grafted on to natural rubber latex alone or in admixture with polybutadiene and/or SBR latex using the process and reaction conditions herein described. In another embodiment styrene alone is grafted on to the base latex. Apart from vinyl aromatic or vinylidene aromatic monomers and unsaturated nitrile monomers, a lower ester of an unsaturated carboxylic acid, e.g., methyl or ethyl methacrylate or methyl or ethyl acrylate may be employed preferably in amounts not exceeding 60% by weight of the monomer mixture. In general it will replace all or part of the unsaturated nitrile.

The latex is preferably imbibed with the monomer(s) at a temperature of 20° to 90° under continuous flow conditions, prior to grafting. Generally the imbibition time is 30 to 90 minutes, preferably up to 50 minutes. The preferred imbibition temperature is 50° to 70°C.

The reaction is carried out in two agitated reactors which are preferably connected in cascade. The reactors may be cooled as required to keep the temperature of each reactor within the required temperature range. Preferably the reaction is carried out rapidly, i.e., the conversion of monomer to polymer is at least 0.5% per minute whilst not exceeding the conversion rate of 5% per minute. In one embodiment our invention is carried out under substantially adiabatic conditions retaining 70% or more of the heat of polymerisation in the reaction mixture, adjusting other factors in the system e.g., solids content, to keep the temperature in the required range. Generally the total reaction time (excluding any imbibition period) is 30 to 45 minutes. The solids content of the latex-monomer mixture is generally 25 to 35% (calculated solids content at the end of the reaction).

The conversion of monomer to polymer in the first reactor is high, generally at least 50%. Preferably it does not exceed 65%.

The grafted latex is removed continuously from the second reactor, the overall conversion of monomer to polymer being at least 85% and preferably is at least 95%.

Any type of natural rubber latex may be used as base latex for grafting using the reaction conditions herein described. In other words a low ammonia latex or

high ammonia latex is suitable. There may be advantage in centrifuging the natural rubber latex before use to obtain optimum particle size for grafting. Adjustment of particle size may be achieved by other methods known in the art.

The grafted latex may be used as such but preferably it is coagulated and dried to form a crumb. This crumb is advantageously blended with a copolymer of styrene and acrylonitrile to form an impact resistant thermoplastic. If desired, the grafted latex and any unreacted monomer(s) may be aged in a separate vessel after removal from the second reactor.

Where a blend of natural rubber latex and a compatible latex, e.g. SBR or polybutadiene latex, is used as the backbone, the amount of compatible latex is normally not more than 50% by (dry) weight of the blend, although greater amounts, e.g. up to 70% or even 90%, may be used.

Examples.

All parts and percentages are by weight.

A series of graft copolymers of styrene (40 parts) and styrene-acrylonitrile (27 and 13 parts) on to natural rubber latex (60 parts dry weight) are prepared in the laboratory using the following procedure.

The monomer(s) and the latex at a calculated solids content of 25% are imbibed with added emulsifier at 50°C for a period of 30 minutes under continuous flow conditions by continuous metering of the monomers and the latex to a stirred vessel. Tert dodecyl mercaptan modifier (0.15 parts) was added with the monomers to the imbibition vessel.

Reaction mixture is continuously removed from this agitated vessel and supplied with polymerisation initiator to a first reactor (R1). Reaction mixture is continuously removed from the first reactor vessel to a second reactor (R2) wherein polymerisation is continued. Grafted latex is removed from the second reactor and is coagulated, washed and dried. Both reactors are equipped with a high speed stirrer and the reaction conditions used are given in Table 1.

In the case of grafting of styrene alone, the initiator used is tert-butyl hydroperoxide with tetraethylene pentamine. In the case of grafting styrene and acrylonitrile, tert-butyl hydroperoxide with diethylene triamine is used.

In each case the grafted rubber is blended with a styrene acrylonitrile copolymer (SAN) or with crystal polystyrene (PS) in a Brabender (Trade Mark) plastograph to give thermoplastic compositions containing the percentage grafted rubber indicated in Table 2. Samples are moulded into $\frac{1}{4}$ inch (3.2 mm) samples and the impact strength and hardness measured. Results are indicated in Table 2.

TABLE 1.

Ex.	Monomer(s)	Emulsifier	Temp. (°C)	Conversion
1	S/AN	Potassium Oleate	(0.6) R1 60 R2 70	65%—70% 94%
2	S/AN	Potassium Oleate	(0.3)	
		Bevaloid*	(0.3) R1 60 R2 70	65%—70% 95%
3	S/AN	Potassium Oleate	(0.6) R1 60 R2 70	65%—70% 98%
4	S/AN	Potassium Oleate	(0.3)	
		Bevaloid*	(0.3) R1 60 R2 70	65%—70% 91%
5	S	Potassium Laurate	(0.2) R1 40 R2 45	55%—60% 95%

Note: No modifier was used in Examples 3 and 5.

*Bevaloid is a registered Trade Mark and is the sodium salt of a naphthalene-sulphonic-acid-formaldehyde condensate.

S = Styrene. AN = Acrylonitrile.

The reaction time was 45 minutes (Examples 1 to 4) and 30 minutes (Example 5).

TABLE 2.

Ex.	% graft rubber	Impact Strength (ft lbs/inch)	Hardness
1	20	3.1	97
2	18	2.5	105
3	20	4.5	101
4	20	4.9	93
5	20	5.8	76

In Examples 1 to 4 SAN was used in the blend and in Example 5 Polystyrene.

WHAT WE CLAIM IS:—

1. A continuous process for grafting natural rubber latex comprising (1) supplying the latex, one or more vinyl or vinylidene monomers to be grafted and polymerisation initiator to a first agitated reactor; (2) carrying out a proportion of the graft reaction in the first reactor; (3) continuously removing reaction mixture from the first reactor to a second agitated reactor; (4) continuing the graft reaction in the second reactor to a conversion of at least 85% by weight of the monomers to polymer and (5) removing the grafted latex from the second reactor, the conversion in the first reactor not exceeding 75%, the temperature of each reactor being from 40° to 100°C.
2. A process according to Claim 1 wherein the temperature of each reactor is 50° to 65°C.
3. A process according to Claim 1 or 2 wherein the temperature of the second reactor is higher than that of the first.
4. A process according to any preceding claim wherein the rate of conversion of monomer to polymer is in the range 0.5% to 5% per minute.
5. A process according to any preceding claim wherein the conversion in the first reactor does not exceed 65%.
6. A process according to any preceding claim wherein the latex is imbibed with the monomers at a temperature of 20° to 90°C under continuous flow conditions prior to grafting.
7. A process according to Claim 6 wherein the imbibition time is 30 to 90 minutes.
8. A process according to Claim 6 or 7 wherein the imbibition temperature is 50° to 70°C.
9. A process according to any preceding claim wherein the natural rubber latex is used blended with up to 50% by weight based on the dry weight of the blend of a compatible rubber latex.
10. A process according to Claim 9 wherein the natural rubber latex is used blended with polybutadiene or styrene-butadiene rubber latex.
11. A process according to any preceding claim wherein the latex is grafted with one or more vinyl aromatic monomers.
12. A process according to any one of claims 1 to 10 wherein the latex is grafted with one or more vinyl aromatic monomers and one or more unsaturated nitrile monomers.
13. A process according to claim 12 wherein the latex is grafted with styrene and acrylonitrile.
14. A process according to any preceding claim substantially as described in the Examples.

For the Applicants,
CARPMAELS & RANSFORD.
Chartered Patent Agents.
43 Bloomsbury Square,
London, WC1A 2RA.